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THERMAL TREATMENT OF IRON–COPPER METASTABLE ALLOYS

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Abstract

Mechanical alloying is a versatile technique for the solid state synthesis of many materials, including alloys such as iron–copper where the elements are immiscible under equilibrium conditions. The structural and magnetic state of these alloys, and their thermal stability, have been investigated by means of thermomagnetometry, DSC, X-ray diffraction and Mössbauer spectroscopy.

Comparison of the thermomagnetometry curves for the various alloys together with analysis of intermediate reaction products enabled the individual thermal processes to be identified. The Curie temperature of the alloys was measured, and it was found that on heating the metastable alloys underwent phase segregation between 300–400°C.

Keywords: copper, iron, mechanical alloying, Mössbauer spectroscopy, thermomagnetometry

Introduction

High energy mechanical alloying has the capacity to produce alloys of elements that are not normally miscible under equilibrium conditions. Iron–copper is one of the most interesting of these normally immiscible systems, since it is possible to produce a solid solution alloy across the composition range, the structure and magnetic properties of which depend on the relative iron to copper concentration. The formation of the alloy during milling and its structure have been fully investigated [1–3]. This paper, however, concentrates on the study of the thermal decomposition of this system.

Given that alloys of this nature are metastable, they could be expected to phase segregate on heating to form crystallites of elemental iron and copper. A nanocrystalline mixture such as this, of a magnetic and non-magnetic element, is known to exhibit giant magnetoresistive (GMR) effects, where the electrical resistance of the material can be altered by the application of a magnetic field [4–6]. In order to optimise the GMR properties it would therefore be useful to characterise in detail the structural and magnetic changes that occur during thermal treatment of the alloy, and investigate the point at which this phase segregation occurs.

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Experimental

Sample preparation

The milling was carried out using a Fritsch Pulverisette high energy planetary ball mill, with Syalon (Si_3N_4) bowls and balls. Approximately 8 g of sample was used in each case, and the milling containers were sealed in an argon atmosphere to prevent oxidation. The milling disc rotation frequency was set to 600 rpm and to prevent excessive heating the mill was operated for periods of two-hours interspersed with cooling down periods of one hour.

Syalon containers were chosen in preference to the more common stainless steel in order to eliminate the possibility of iron based impurities from the steel affecting the final sample compositions, or showing up independently as contaminants in the Mössbauer spectra. The Syalon containers do wear during the course of a prolonged milling experiment, introducing up to 8 at% Si_3N_4 impurities into the sample according to EDAX measurements. These impurities, however, are immiscible with the sample material and thus do not affect the resultant structural and magnetic properties, in contrast to iron from stainless steel.

The progress of alloying with milling time was monitored, by regularly removing sample material and studying its structure by X-ray diffraction and Mössbauer spectroscopy. From these measurements it was concluded that a milling time of up to 70 h was necessary to ensure complete alloy formation, where this was possible. The results discussed here refer to those samples milled for the full 70 h.

Sample characterisation

The properties of the as-made samples were studied by means of X-ray diffraction and Mössbauer spectroscopy. The changes that occurred on heating were monitored using differential scanning calorimetry and thermomagnetometry. Thermomagnetometry is a particularly valuable technique in this respect as it enables the Curie temperature as well as the decomposition temperature of the materials to be measured. The technique itself involves arranging a magnet below the sample crucible of a standard TGA apparatus, thus providing a magnetic force on the sample [7]. If there are changes in the magnetic state of the sample during heating there will be a change in the force exerted on it and thus a change in the apparent mass. These apparent mass changes will be measured by the TGA in addition to any real changes in mass of the sample.

In the case of Fe–Cu, however, there should be no real changes in the total mass of the sample during thermal treatment, apart from a small increase due to unavoidable oxidation. Thus any changes seen in the thermomagnetometry curves are magnetic, for example the phase segregation of a paramagnetic Fe–Cu alloy into copper and ferromagnetic iron. To link the effects seen with real changes, XRD measurements were made not just of the initial and final products, but also of samples that had been heated to intermediate temperatures.

XRD data were collected on a Philips X-Pert diffractometer in θ-2θ geometry with CuK_α radiation. ^{57}Fe Mössbauer spectra were collected with a Wissel constant acceleration transducer. A triangular waveform was used, and spectra were folded to remove baseline curvature. Calibration was carried out with respect to α-iron at room temperature.

DSC measurements were made with a Shimadzu DSC-50 at a heating rate of 20°C min^{-1}. Thermomagnetometry data were collected using a Perkin-Elmer TGA7, with the PE calibration magnet used to provide the magnetic force. Samples for the DSC and TG experiments were of approximately 20 mg mass and were placed in open platinum crucibles. An atmosphere of flowing nitrogen (flow rate of 60 ml min^{-1}) was used to minimise sample oxidation.

Results and discussion

The initial magnetic state of the Fe–Cu alloys was investigated by means of Mössbauer spectroscopy, with the results shown in Fig. 1. The spectra of those alloys with an iron concentration less than 30 at% comprised one doublet, indicative of a paramagnetic material. (The presence of the doublet and absence of the characteristic sextet of α-Fe also serves to confirm that full atomic level alloying has taken

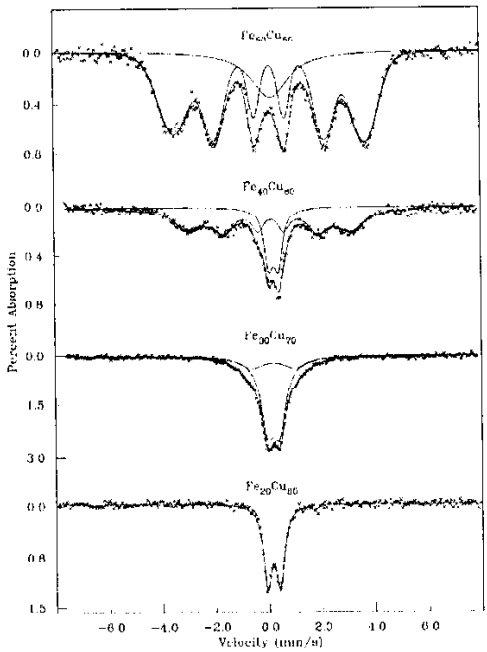

Fig. 1 Room temperature Mössbauer spectra of mechanically alloyed Fe–Cu. The solid lines are least squares fits to the data

place.) With a larger iron concentration, the spectra contained an increasing ferromagnetic sextet component, the hyperfine field of which increased with the proportion of iron in the samples. The large observed linewidths, and the mixture of a ferromagnetic and paramagnetic signal, result from variation in the local structural environment of each iron nucleus. This is caused by the different possible combinations of iron and copper nearest neighbour atoms which can be found in a random substitutional solid solution [8].

The variation in the initial bulk magnetic state of the alloys can also be seen in the thermomagnetometry curves (Fig. 2). The difference between the starting mass of each sample before and after the magnet is applied gives a qualitative measure of the magnetisation of the alloy. The paramagnetic $Fe_{20}Cu_{80}$ shows no change, whereas the ferromagnetic $Fe_{40}Cu_{60}$ and $Fe_{50}Cu_{50}$ both show substantial increases in apparent mass of 34%.

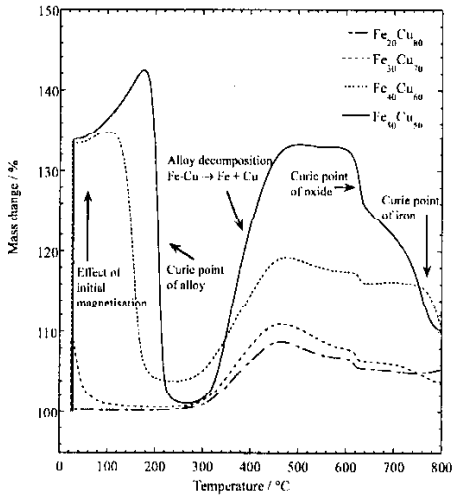

Fig. 2 Thermomagnetometry curves of Fe–Cu alloys. The starting mass is defined as the initial mass of the sample before the magnet is applied

$Fe_{30}Cu_{70}$ shows a small increase in apparent mass of 9%, but this effect disappears almost immediately as heating begins. The disappearance is consistent with a ferromagnetic to paramagnetic transition and indicates that the sample is very close to its Curie point at room temperature, an observation that is supported by its Mössbauer spectrum, which was a doublet with broadened edges that would be expected for a borderline ferromagnetic/paramagnetic material.

The $Fe_{40}Cu_{60}$ and $Fe_{50}Cu_{50}$ samples exhibit losses in mass analogous to that seen in $Fe_{30}Cu_{70}$, but at the higher temperatures of 160 and 220°C respectively. These can also be explained by Curie point magnetic transitions, and indicate, therefore, that the Curie temperature of the Fe–Cu alloy system increases with the iron concentra-

tion. Ultimately, as the iron concentration increases further, the Curie temperature would tend towards that of pure iron.

All the Fe–Cu samples then together exhibit an increase in apparent mass on continued heating from 320–440°C, the magnitude of the increase being greater for the materials with higher iron levels. This change can be associated with the segregation and decomposition of the metastable Fe–Cu alloy to separate iron and copper particles. An increase in apparent mass is seen, since the Fe–Cu alloy is paramagnetic at 320°C, whereas the decomposition product, i.e. elemental iron, is still ferromagnetic. The Curie point of the resulting iron can be seen at 770°C, as expected.

The permanent nature of the phase segregation of the alloy was highlighted by reheating the $Fe_{50}Cu_{50}$ residue. The resulting thermomagnetometry curve remained flat up to 500°C, with the signal from both the Curie point transition of the alloy and its subsequent phase segregation being absent.

The occurrence of phase segregation between 320–440°C is supported by DSC and XRD measurements. The DSC curve of $Fe_{50}Cu_{50}$ (Fig. 3) shows exothermic peaks in this temperature region which can be associated with the phase segregation, together with a peak at higher temperatures that is related to the subsequent recrystallisation and growth of the elemental grains. In previous work [9] it has been shown that in milled materials such as $Fe_{50}Ag_{50}$ where there is little or no alloying during milling, the lower temperature feature in the DSC curve is absent. By comparison, samples such as $Cu_{50}Ag_{50}$, which alloy but are much less thermally stable than $Fe_{50}Cu_{50}$, have an exothermic DSC trace that begins at only 100°C.

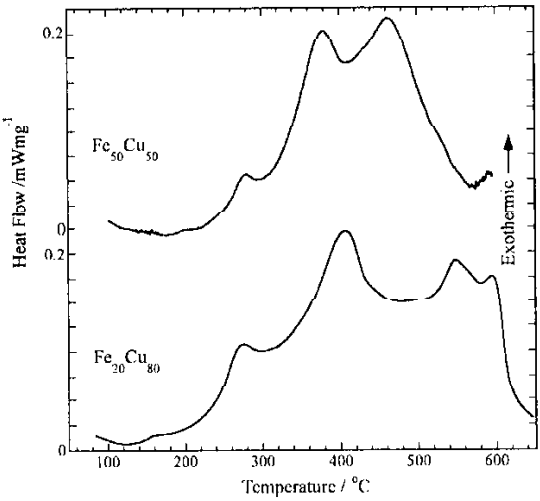

Fig. 3 Differential scanning calorimetry curves for $Fe_{20}Cu_{80}$ and $Fe_{50}Cu_{50}$

The XRD pattern of a $Fe_{50}Cu_{50}$ sample that had been heated to 340°C and then quenched confirms that phase separation has commenced at this temperature

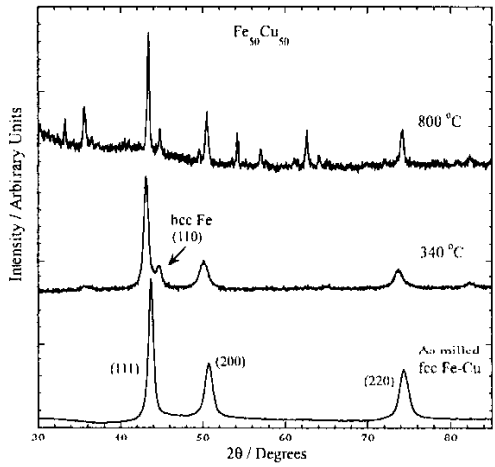

Fig. 4 X-ray diffraction patterns of $Fe_{50}Cu_{50}$ as milled, and after heating to 340 and 800°C

(Fig. 4). The initial fcc structure of the alloy had begun to separate into elemental bcc-Fe and fcc-Cu. There is little difference between the lattice parameter of the fcc Fe–Cu alloy and pure copper, (as expected given that copper and iron are of similar atomic radii), but the phase separation can be seen most distinctly by the emergence of the characteristic bcc-Fe. The width of the XRD peaks is still broad, firstly since the elemental segregation is only partially complete at this temperature, and secondly because further heating is required to eliminate lattice defects and encourage recrystallisation and grain growth.

The XRD pattern of the final product, heated to 800°C shows that, despite an atmosphere of flowing nitrogen in the TGA apparatus, some oxide is present, mainly in the form of magnetite. Magnetite has a Curie temperature of 585°C [10] and so this transition would explain the apparent mass loss seen in the thermomagnetometry curves of all the Fe Cu samples at this temperature.

Oxidation itself can be measured as a real mass change, as opposed to the features described so far in the thermomagnetometry curves, all of which are related to magnetic changes in the sample. The difference between the starting and final mass of the sample (without the magnet in place) gives a value for the oxygen uptake during heating, approximately 6 wt% in the case of $Fe_{50}Cu_{50}$. A separate sample of $Fe_{50}Cu_{50}$ was heated in the TG, under the same conditions as before, but without the magnet being present. It was seen that the oxidation occurs gradually throughout most of the temperature range, which explains why no specific feature corresponding to an oxidation process was seen in the original thermomagnetometry curves.

Conclusions

It has been shown that solid solution alloys of iron-copper can be formed through high energy ball milling, even though these elements are normally immiscible under

equilibrium conditions. The resulting alloys are metastable, and decompose on heating to give grains of elemental iron and copper. Thermomagnetometry has been used to give a temperature range of 300–400°C for phase segregation in this system, with the resultant change in structure being confirmed by X-ray diffraction. Thermomagnetometry measurements have also highlighted the variation in Curie temperature of the Fe–Cu alloy with changing iron to copper ratio.

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